Testing of Innovative Fe- and Ca-Mn-based Oxygen Carriers with Natural Gas in Continuous Operation

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Summary

Chemical-looping combustion (CLC) of gaseous fuels, such as natural or refinery gas, could be a viable option in a variety of industries for production of heat and electricity with CCX. Further, CLC can be combined with conventional steam-methane reforming for efficient carbon-neutral hydrogen production. A series of collaborative European projects have been carried out since 2002, which focused on oxygen-carrier development and upscaling of both the CLC process and oxygen-carrier production with sulfur-free natural- and refinery gases as fuel. In the latest project, SUCCESS (2013-2017), a series of oxygen carriers based on Fe and Ca-Mn materials were developed using commercial and low-cost raw materials. Two commercial methods for particle production were used: impregnation of Fe 2O 3 on Al 2O 3 and spray-drying of CaMnO 3. These two oxygen carriers were tested using a continuously operating laboratory-scale unit, which has a nominal fuel input of 10 kW. In this unit, the gas velocities in the riser and in the grid-jet zone of the gas distributor come close to gas velocities of industrial-scale units and the material is exposed to a large number of redox cycles. Both materials functioned well during operation with natural gas, with low agglomeration. Although the degree of particle elutriation was high for both materials, the actual fines production (< 45 µm) was high only initially, but decreased as a function of time.

Conclusions

• A series of oxygen-carrier particles based on CaMnO 3 (C14, C28) were produced up to multi-ton scale using spray-drying. It was found that the perovskite structure is simple to produce, also with highly heterogeneous and low-grade raw powders.
• The important CLOU property was seen for all Ca-Mn-based oxygen-carrier materials produced.
• Several of the Ca-Mn-based oxygen-carrier materials produced with substitute raw materials could match the performance of the reference materials produced with high-purity raw materials, and several oxygen carriers showed a combination of high reactivity and low attrition.
• For the impregnated Fe-based material, the gas yield was less than 85%, even at specific solid raw materials inventories of more than 1000 kg/MW e.
• For the CaMnO 3-based materials, the expected lifetime is 700-12 000 h, and for the Fe-based oxygen carrier, the expected lifetime was around 700 h.

Development route (Ca-Mn-based OCs)

Fe-based, impregnated OC
Fuel input 3.2-5.8 kW e Fuel-reactor temp. 900-970°C Gas vel. in Riser 1.4-1.7 m/s Solids inventory 9-12 kg Spec. FR bed mass 620-1650 kg/MW e

Ca-Mn-based, spray-dried OC (2 OCs)
Fuel input 1.2-8.9 kW e Fuel-reactor temp. 850-980°C Gas vel. in Riser 1.9-2.9 m/s Solids inventory 8-16 kg Spec. FR bed mass 320-2300 kg/MW e

Development route

Fe-based, impregnated OC
1. Air reactor (ID 150 mm)
2. Riser (ID 80 mm, Htot 2.2 m)
3. Cyclone
4. Air reactor (ID 80 mm, Htot 2.2 m)
5. Air reactor (ID 150 mm)
6. Lower loop seal
7. Loop-seal (fuel gas/nitrogen)
8. Fuel reactor (ID 80 – 180 mm)
9. Cyclone
10. Lower loop seal
11. Loop-seal (fuel gas/nitrogen)

Ca-Mn-based, spray-dried OC (11 OCs)
Fuel input 180-300 kW e Fuel-reactor temp. 850-975°C Gas vel. in Riser 0.7-1.0 m/s Solids inventory 310-400 g Spec. FR bed mass 225-540 kg/MW e

Experimental details

Chemical-looping combustion

• Two interconnected fluidized-bed reactors
• No exchange of gas between reactors, i.e., air and fuel are not mixed.
• Oxygen is transported to the fuel by a solid oxygen carrier, which is cyclically oxidized and reduced.
• Net heat of reaction is the same as for regular air combustion, i.e., there is no energy penalty for separation of CO 2.

Raw-material substitution

Results

Up-scaling

CH 4 conversion at 900°C in 300 W reactor

CH 4 conversion at 10 kW reactor

Experimental parameters

• Chemical-looping combustion